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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO) 10 April 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-078**
Fajardo, Mario, "Chemistry and Spectroscopy in Solid Parahydrogen"

U. Wyoming Chemistry Dept. Seminar **(Statement A)**
(Caramie, WY, 20 April 2001) (**Deadline: 20 April 2001**)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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PHILIP A. KESSEL Date
Technical Advisor
Space & Missile Propulsion Division

Department of Chemistry, University of Wyoming, Laramie, WY, 20 April 2001

Chemistry and Spectroscopy in Solid Parahydrogen

Mario E. Fajardo

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* Cryosolid Propellants Team
* HEDM Cryosolid Propellants Concept (Atoms in Solid Hydrogen)
* Rapid Vapor Deposition of <u>Transparent</u> Parahydrogen (pH_2) Solids
* B and Al Doped pH_2 Solids
* High Res. IR Spectroscopy of Molecular Dopants in Solid pH_2
* Summary

Cryosolid Propellants Team

* Mario E. Fajardo, Michelle E. DeRose, and Simon Tam
  Bill Larson (thermal B atom source)

* Jeff Sheehy, Jerry Boatz, Peter Langhoff (in-house theory)

* AFOSR Contractors:
  - P. Dagdigian @ Johns Hopkins: Al/H_2 & B/H_2 Complexes
  - M. Alexander @ U. Maryland: B/H_2 Interaction Potentials
  - G. Voth @ U. Utah: Path-Integral Monte Carlo Simulations
  - G. Scoles & K. Lehmann @ Princeton U.: Helium Clusters

* External Collaborators:
  - T. Momose @ Kyoto U.: High Resolution IR Spectroscopy

* Summer Visiting Professors:
  - R.J. Hinde @ U. Tennessee: Dopant-Induced IR Activity
  - D. Anderson @ U. Wyoming: Dopant IR Absorptions

Propellant Performance Figures of Merit

Specific Impulse, I_{sp}:

$$I_{sp} \equiv (\text{total impulse / propellant weight})$$

$$= g_0 \langle v_{exh} \rangle \qquad \text{“seconds”}$$

$$\propto \sqrt{\frac{\langle K.E. \rangle}{m}} \propto \sqrt{\frac{\Delta H}{m}} = \sqrt{\Delta H_{sp}}$$

Density, ρ:

higher density $\Rightarrow$ smaller & lighter tanks

$\Rightarrow$ less aerodynamic drag

$\Rightarrow$ condensed phase propellants

[G.P. Sutton, “Rocket Propulsion Elements” (Wiley, New York, 1992).]

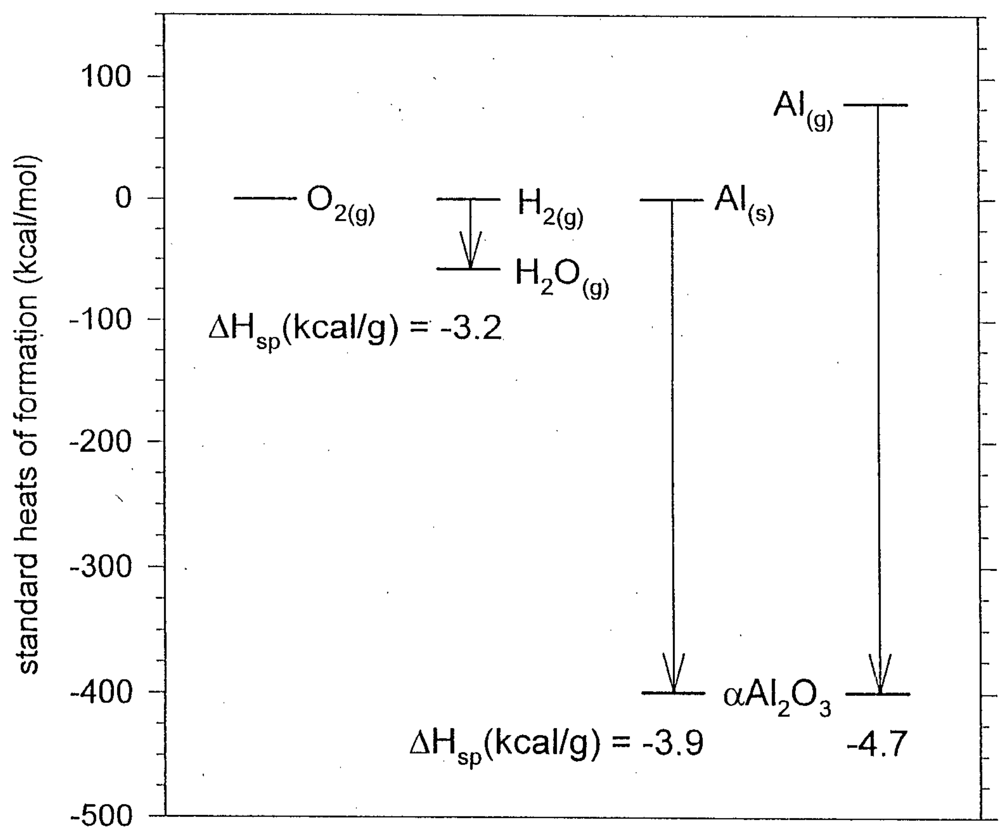
"Revolutionary" vs. "Evolutionary" HEDM Concepts

* "Revolutionary" means better than LOX/LH_2:
  - LOX/LH_2 — $\Delta H_{sp} = 12.6$ MJ/kg (3.0 kcal/g)
  - HEDM Target: — $\Delta H_{sp} > 15.0$ MJ/kg (3.6 kcal/g)

* Early (c1990) Revolutionary HEDM Concepts:
  - tetrahydrogen (H_4)
  - metastable triplet helium (He^* and He_2^*)
  - spin-polarized atomic hydrogen ($H\uparrow$)
  - high-spin species (^5CO)
  - dications (AB^{++}, ABC^{++})
  - ♥ "non-metallics" (*e.g.* O_4/H_2, N_4, N_8, N_{20}) **N_5^+!**
  - metallic hydrogen
  - ♥ metal atoms and clusters in solid H_2

Cryosolid Propellants Concept

Use cryogenic solid hydrogen as a "packaging material" to store energetic species such as metal atoms and clusters.



Atom Additive Payoffs (5 % molar)

Sea level specific impulse, I_{sp}, in seconds (% change)

$P_{chamber}$ = 1000 PSIA, $P_{exhaust}$ = 14.7 PSIA

Additive	in standard state $M(5\%)/LOX/H_2$	as atoms $M(5\%)/LOX/H_2$	monoprop. $M(5\%)/H_2$
none	403		
C	381 (-5%)	515 (+28%)	515 (+28%)
B	407 (+1%)	508 (+26%)	465 (+15%)
Be	427 (+6%)	493 (+22%)	
Si	400 (-1%)	460 (+14%)	
Al	407 (+1%)	454 (+13%)	
H	403	430 (+7%)	380 (-6%)
Li	404	428 (+6%)	
Mg	400 (-1%)	416 (+3%)	

Cryosolid Propellants Objectives

* <u>Make</u> solid hydrogen samples (any size) containing 5% molar concentration of trapped energetic additives.

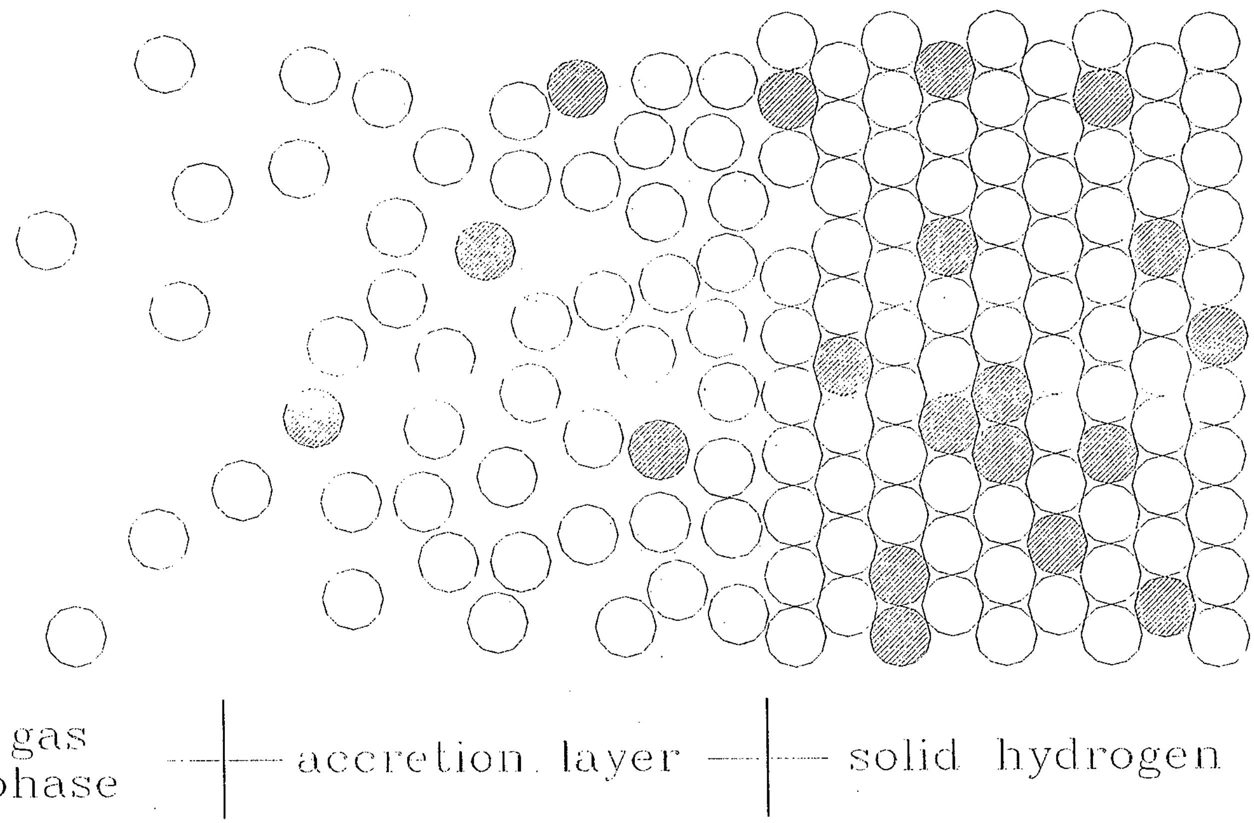
* <u>Measure</u> absolute concentrations of energetic species.

* <u>Scale-up</u> samples; produce ~ 1 cm^3 samples in our lab.

Example: 5% Al/pH_2, $V = 1\ cm^3$
assume each Al atom replaces one H_2 molecule
$\Rightarrow$ 58 mg Al / 83 mg H_2 (*see display item*)
$\therefore\ \rho = 0.142\ g/cm^3$ (+100%)

Cryosolid Propellants Approach

* Rapid vapor deposition of metal atom vapor and pre-cooled parahydrogen gas onto a liquid helium cooled substrate in vacuum.



Dopant Reactions within solid pH_2

* ideally:

$X + pH_2$	$\xrightarrow{T=2K} X/pH_2$	isolated atoms

* in practice:

$X + X + M$	$\rightarrow X_2 + M$	recombination
	$\rightarrow X_n$	
$X + H_2 + M$	$\rightarrow HX + H + M$	reaction
	$\rightarrow H_nX + M$	
$X_n + H_2 + M$	$\rightarrow HX_n + H + M$	both
	$\rightarrow H_mX_n + M$	

Department of Chemistry, University of Wyoming, Laramie, WY, 20 April 2001

The Perils of Calorimetry

TABLE IX

CONCENTRATIONS OF FREE RADICALS REPORTED

Radical	Matrix	Mole per cent radicals	Method of production and estimate[a]	Reference
O	O_2	4–20	Gas, cal	Minkoff *et al.* (1959).
		<3	Gas, IR	Harvey and Bass (1958)
		~ 1	Gas, cal	Broida and Lutes (1956)
OH	$Ca(OH)_2$	0.6	γ, ESR	R. Livingston[b]
N	N_2	4	Gas, cal	Minkoff *et al.* (1959)
		0.2	Gas, cal	Broida and Lutes (1956)
		0.03	γ, ESR	Wall *et al.* (1959b)
		>0.03	Gas, cal	Fontana (1958)
		0.01–0.04	Gas, MS	Fontana[c]
OH(?)	HCOOH	0.2	γ, ESR	Matheson and Smaller (1955)
CH_3	CH_4	0.14	γ, ESR	Wall *et al.* (1959a)
H	CH_4	0.1	γ, ESR	Wall *et al.* (1959a)
N	NH_3	0.1	Gas, ESR	Cole and Harding (1958)
H	$HClO_4$—H_2O	0.1	γ, ESR	Livingston *et al.* (1955)
H	H_2O	0.01	γ, ESR	Matheson and Smaller (1955)
H, NH_2(?)	NH_3	0.01	γ, ESR	Matheson and Smaller (1955)
ROH	Alcohols	~ 0.01	UV, ESR	D. Ingram[b]
H	H_2	0.0006	γ, ESR	Wall *et al.* (1959a)

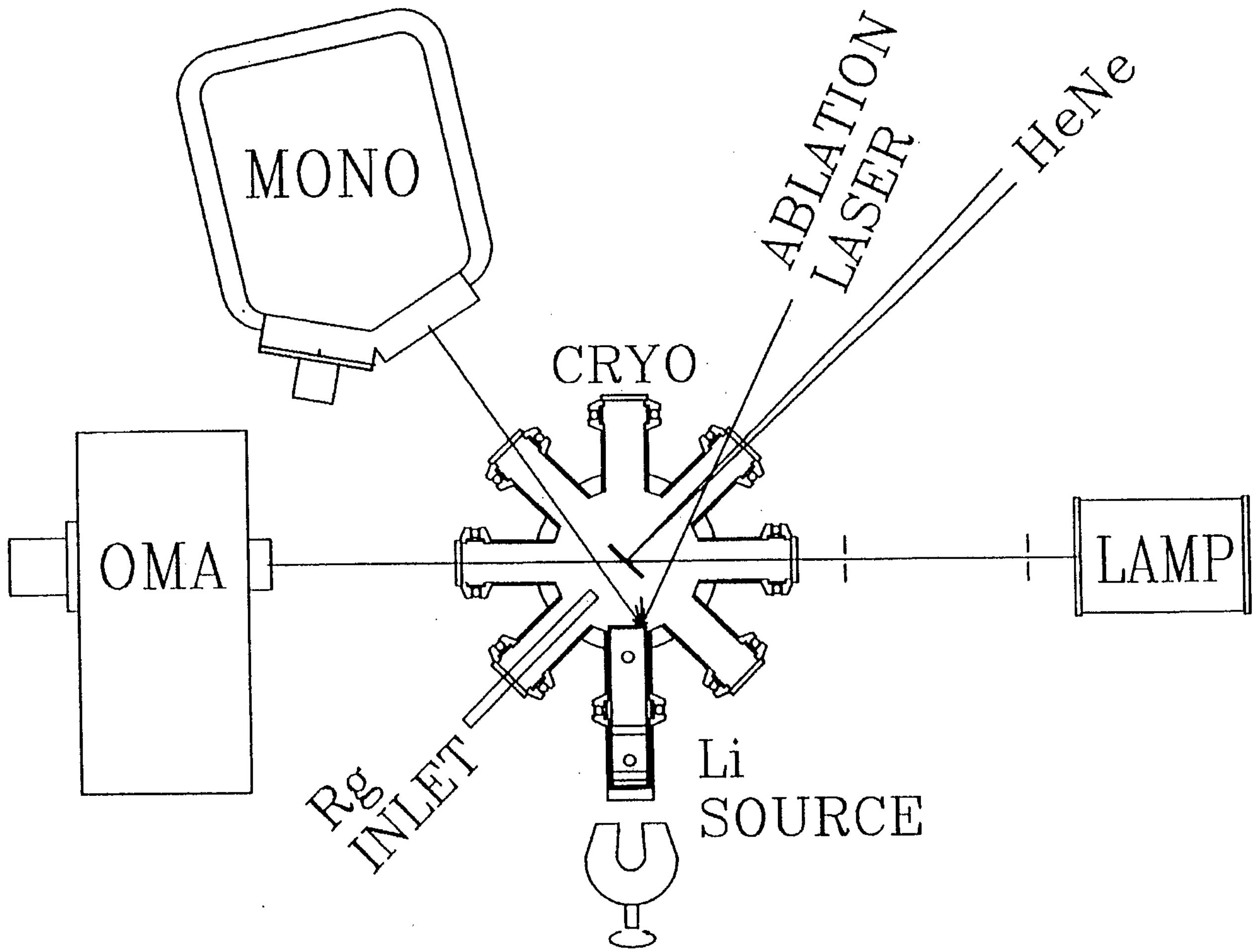
[a] Abbreviations: gas = rapid condensation of gaseous radicals; γ = gamma ray *in situ* production; UV = photolytic *in situ* production; IR = infrared analysis; cal = calorimetry; MS = magnetic susceptibility.

[b] Private communication.

[c] Fontana, B. J. (1959). *J. Chem. Phys.* **31**, 148.

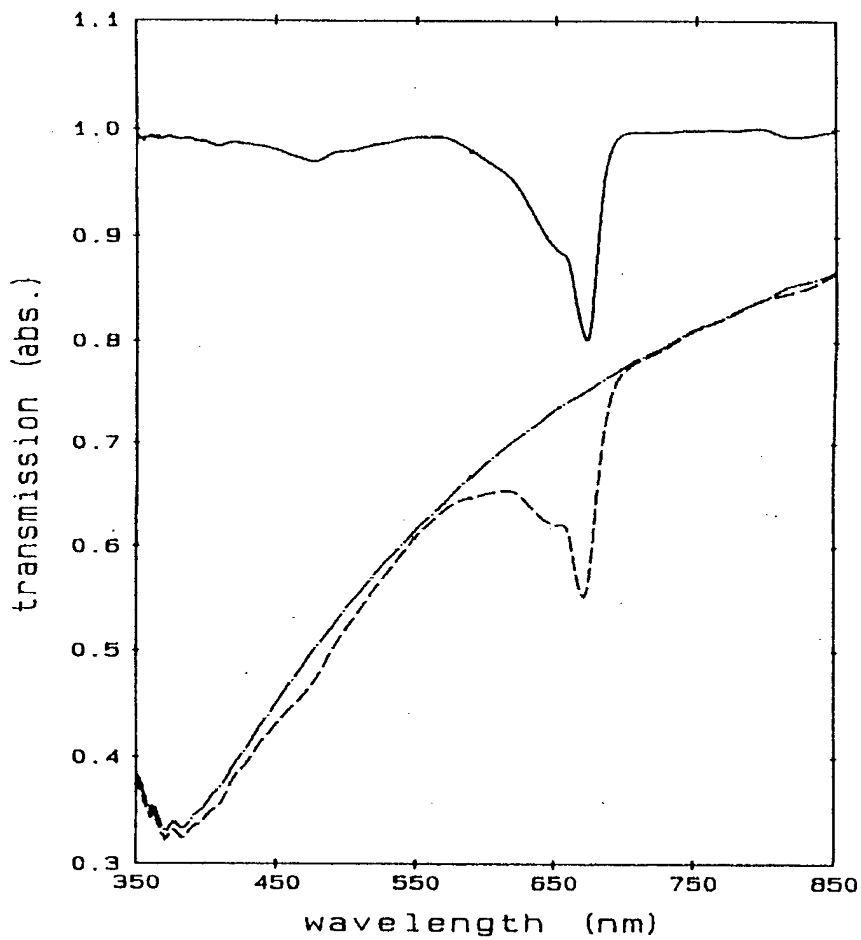
[A.M. Bass and H.P. Broida, "Formation and Trapping of Free Radicals" (Academic, New York, 1960).]

Experimental Diagram (c1993)



M.E. Fajardo, J. Chem. Phys. **98**, 110 (1993).

Transmission Spectrum of Li/nH_2, d ≈ 10 μ



——— difference + 1.0

—·— pure nH_2

------ Li/nH_2

M.E. Fajardo, J. Chem. Phys. **98**, 110 (1993).

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

"There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow."

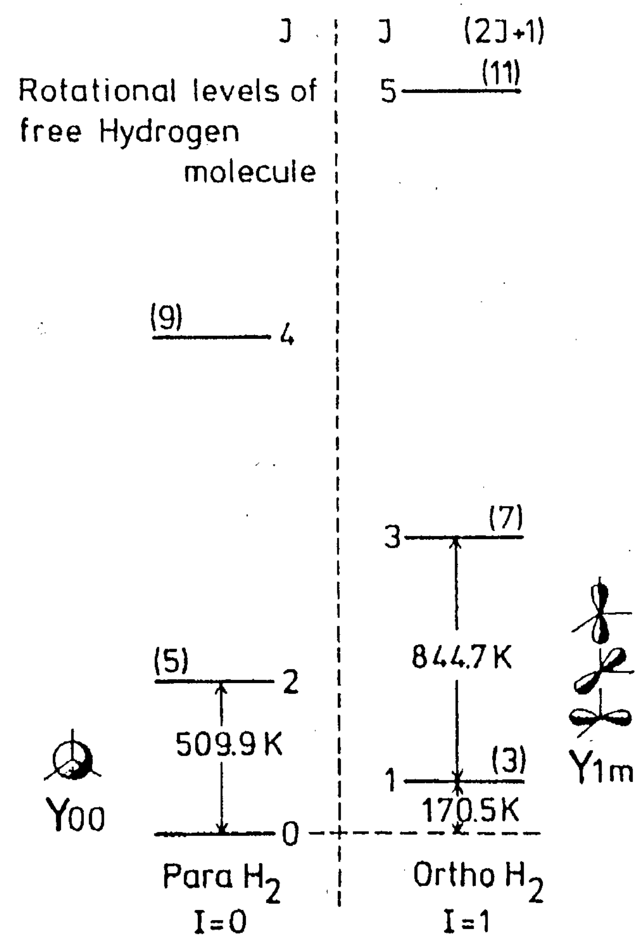
Crystallite Light Scattering (p. 83)

"The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black."

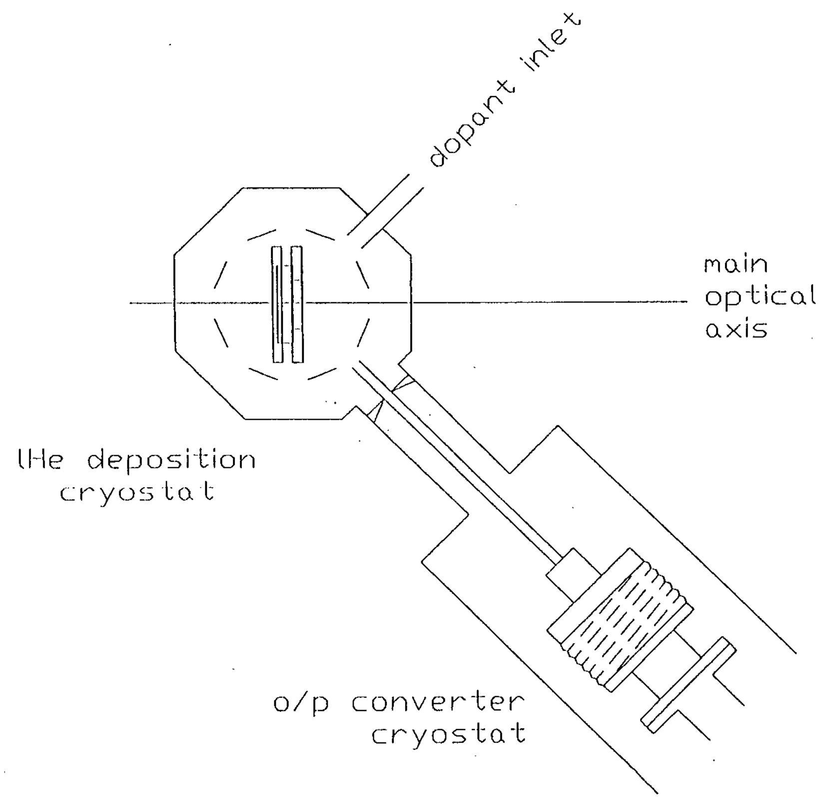
[P.C. Souers, Hydrogen Properties for Fusion Energy (UC Press, Berkeley, 1986)]

ortho- and para-hydrogen



[I.F. Silvera, Rev. Mod. Phys. **52**, 393 (1980)]

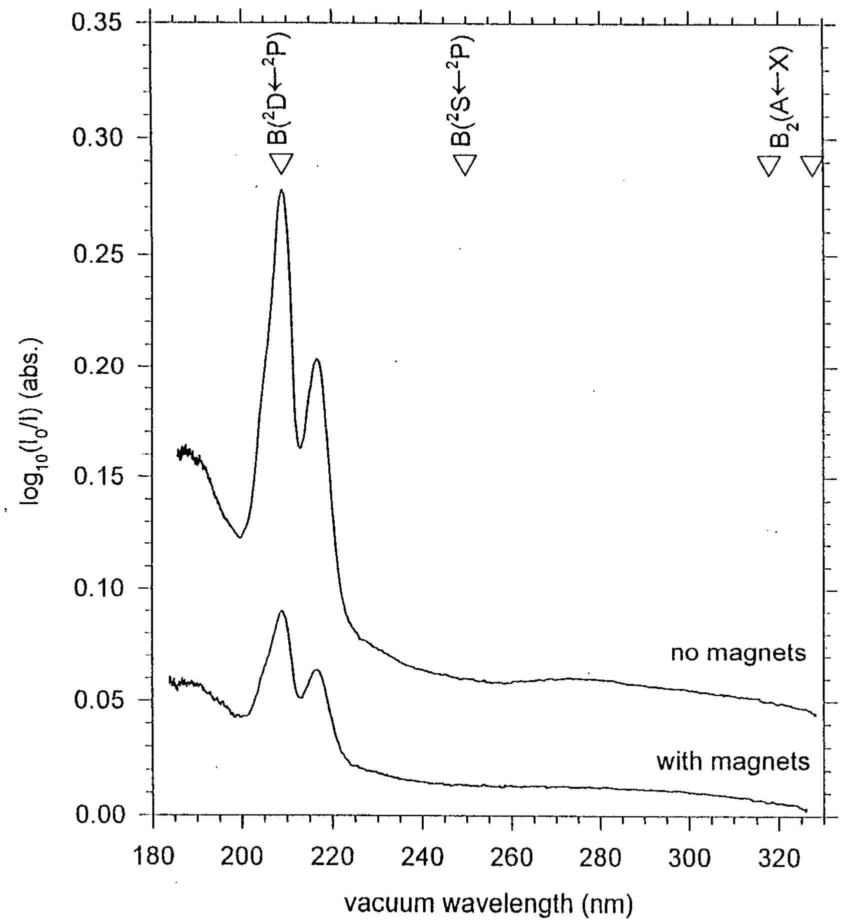
Rapid Vapor Deposition of Gram-Scale Optically Transparent pH_2 Solids (c1997)

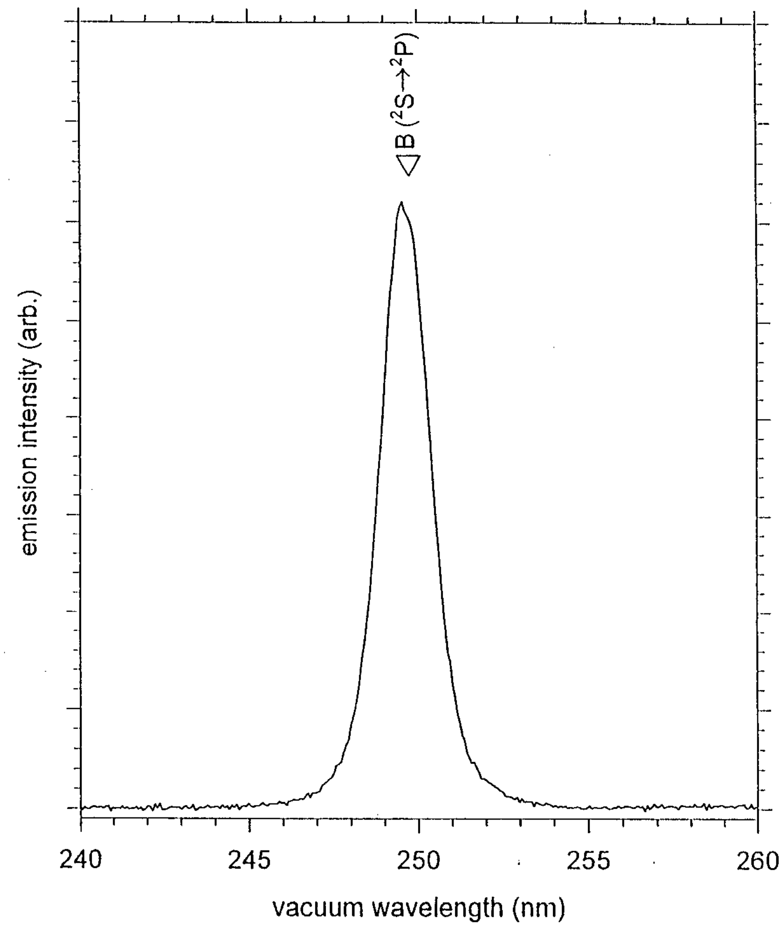


M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).
S. Tam and M.E. Fajardo, Rev. Sci. Instrum. **70**, 1926 (1999).

Department of Chemistry, University of Wyoming, Laramie, WY, 20 April 2001

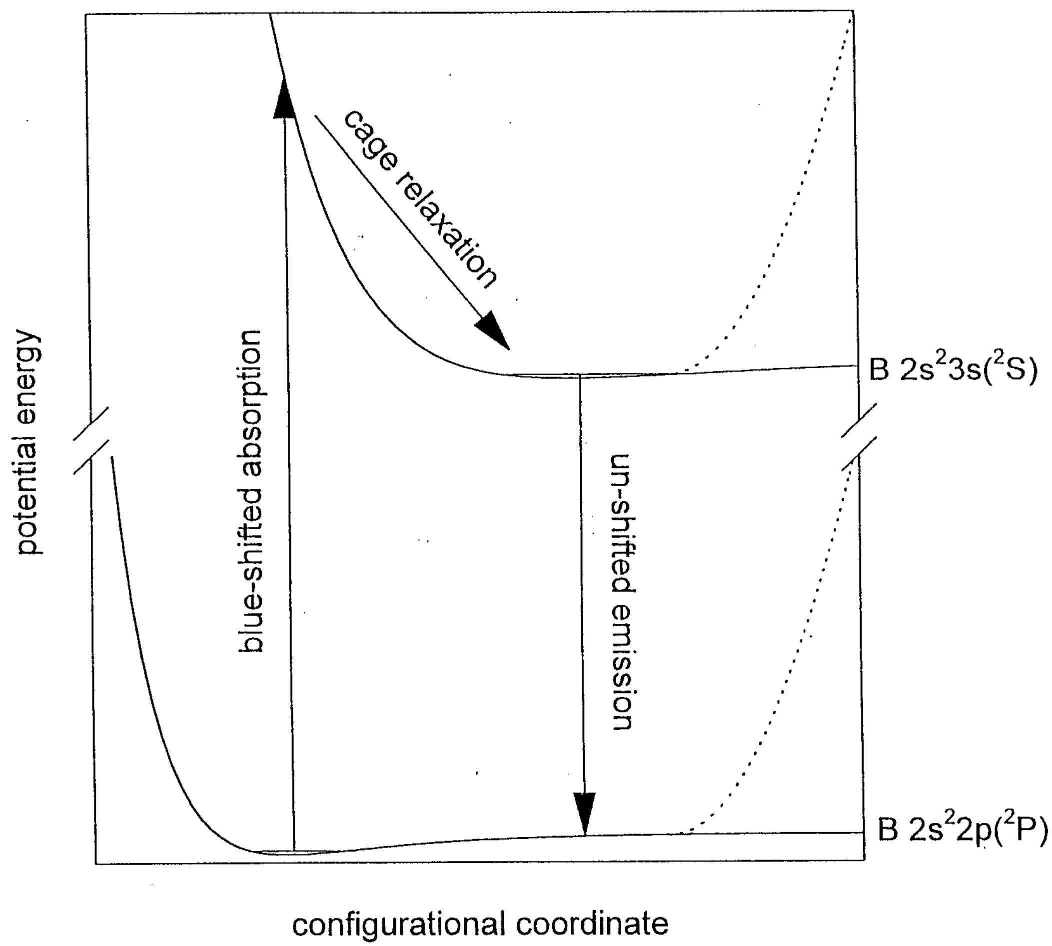
Electronic Spectroscopy of B/pH_2 ($d \approx 2$ mm)





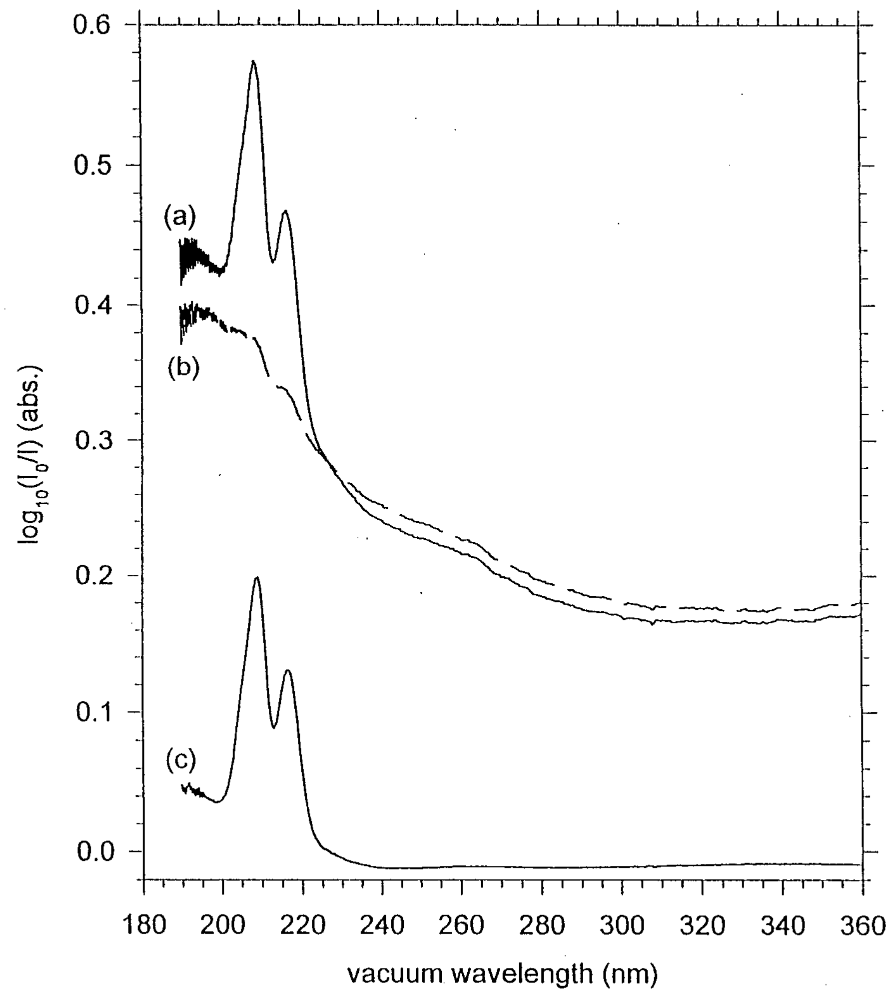
S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, J. Chem. Phys. **113**, 9067 (2000).
[J.R. Krumrine, S. Jang, G.A. Voth, and M.H. Alexander, J. Chem. Phys. **113**, 9079 (2000)]

Photodynamics Cartoon for B/pH_2



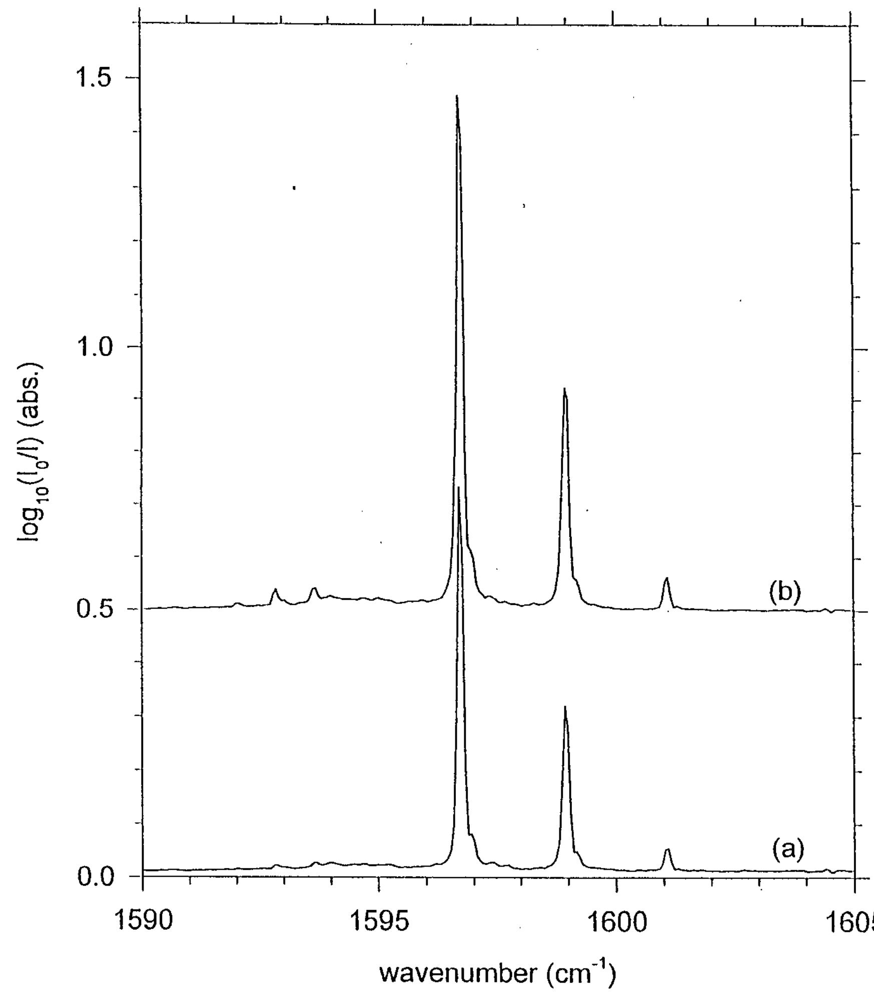
S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, J. Chem. Phys. **113**, 9067 (2000).

Photobleaching of B/pH_2 Absorptions



S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, J. Chem. Phys. **113**, 9067 (2000).

IR Absorption Spectra of B_2H_6/pH_2

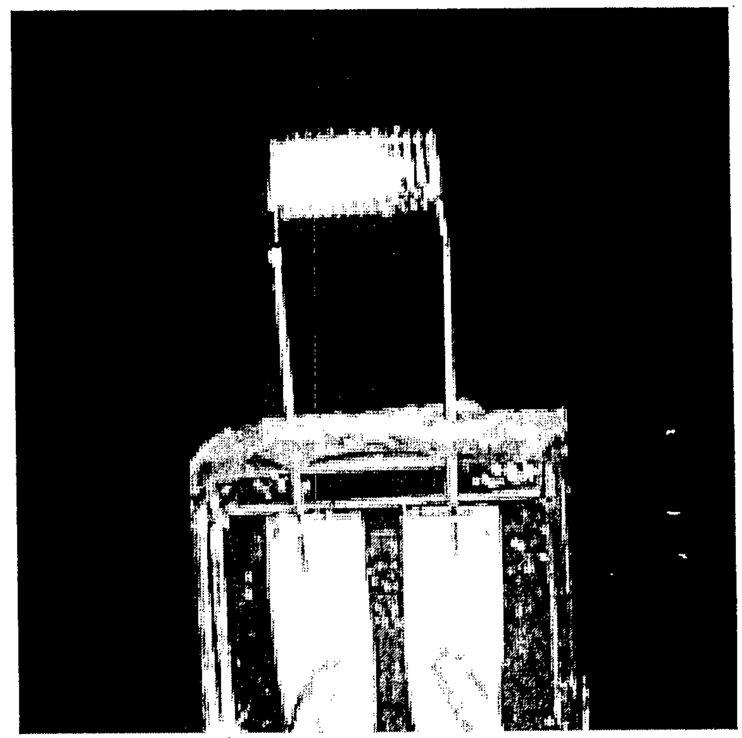


S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, J. Chem. Phys. **113**, 9067 (2000).

Requirement for High Flux HEDM Sources

* A 5 % doping level, and a sample growth rate of 1 mm/hour, require a flux of $\Phi_{HEDM} \approx 3 \times 10^{16}$ #/cm^2-s at the deposition substrate. For Al atoms, this translates to a mass flux of 5.8 mg/cm^2-hour, <u>delivered</u> to the deposition substrate.

* Began FY00 using miniature tungsten filament evaporation sources based on our FY99 effort to produce thermal B atoms.



* <u>Total</u> mass loadings of Al metal were ~ 10 mg, just enough to detect trapped Al atoms in Ar; $\Phi_{Al} \sim 10^{11}$ #/cm^2-s @ R = 5 cm.

High Flux HEDM Sources

* Purchased commercial Al evaporator; PBN crucible holds $\approx$ 10 g Al in horizontal orientation.

* $T_{max} = 1200\ ^{\circ}C \Rightarrow P_{vap}(Al) \approx 8x10^{-3}$ torr $\Rightarrow \Phi_{Al} \approx 10^{18}$ #/cm^2-s

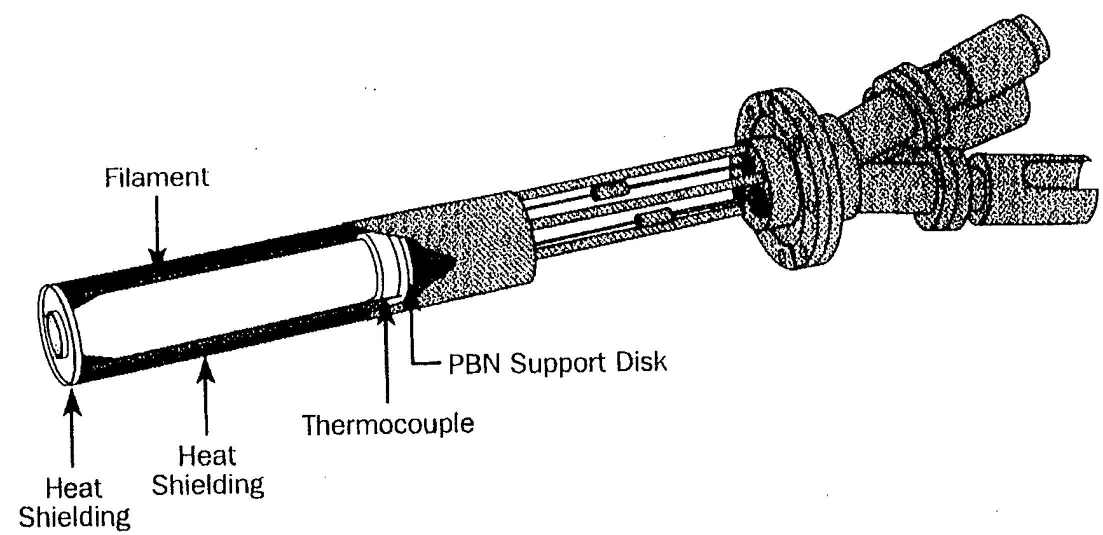
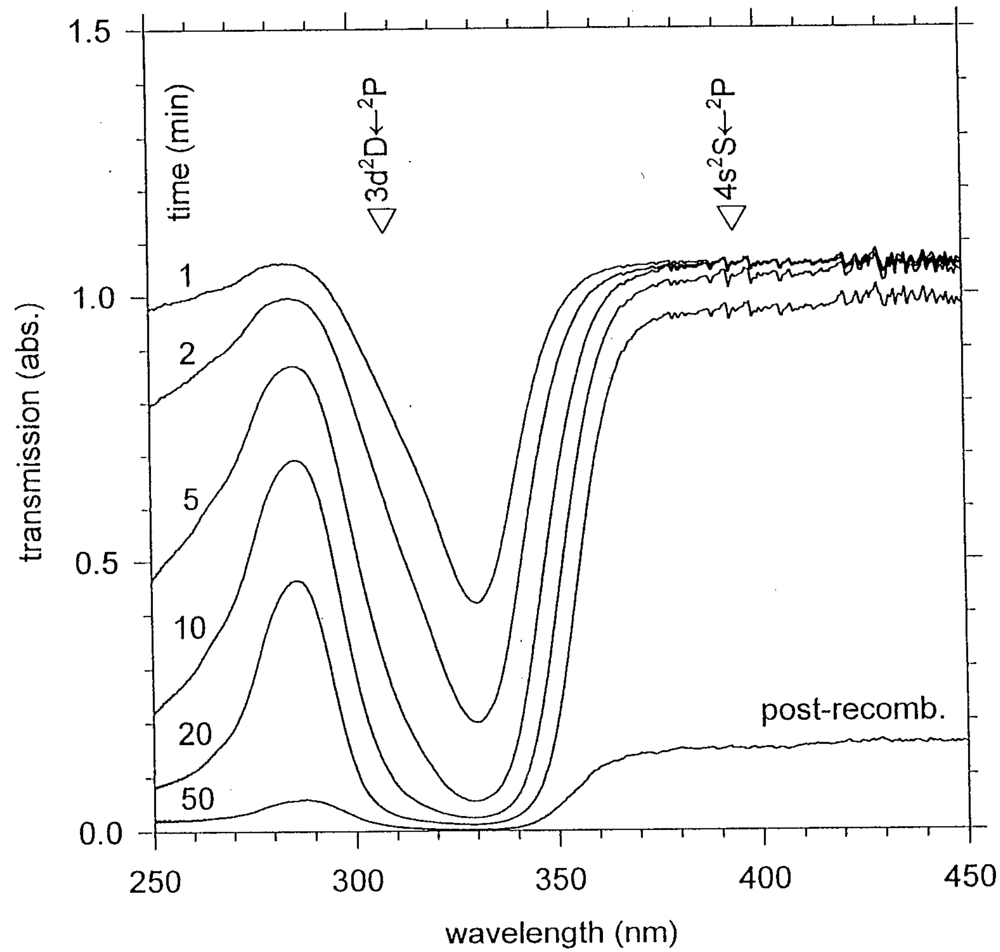


Figure 1-3: Schematic of the EPI SUMO™ Effusion Cell.

UV Spectroscopy Al/pH_2

* Al atom UV absorption saturates at high column densities.



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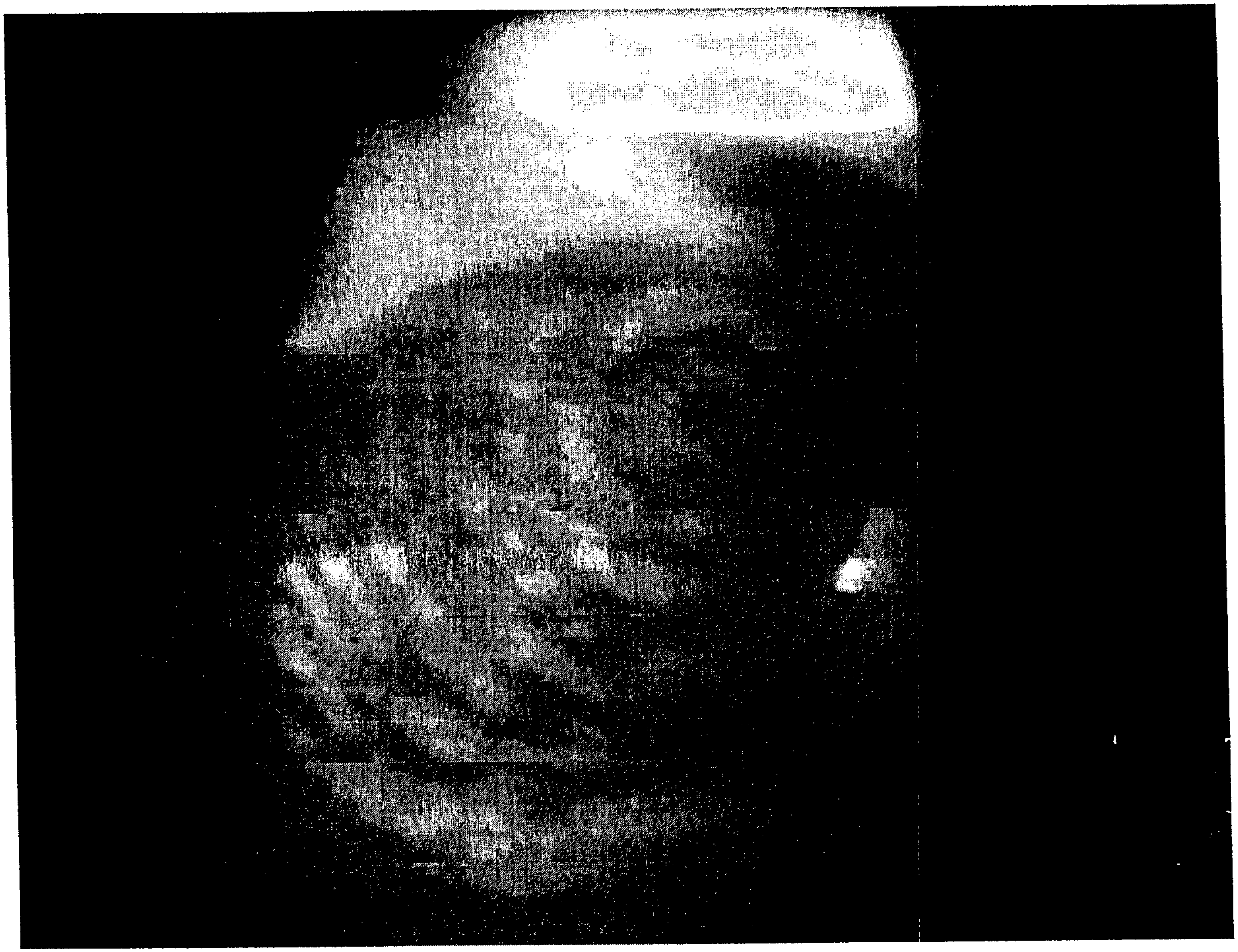
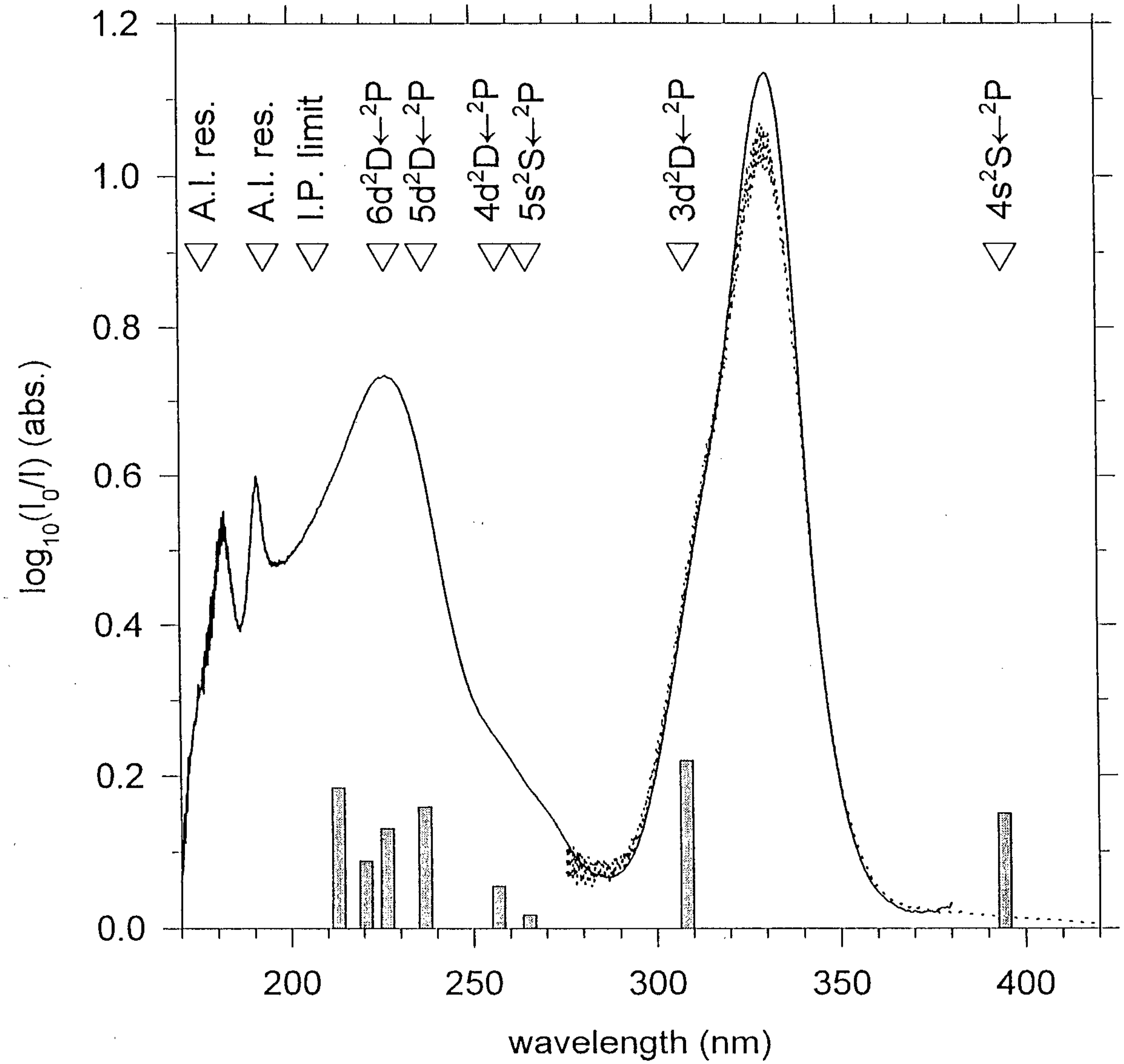
Recombination/reaction in Al/pH_2



Assignment of Al/pH_2 UV Absorptions



High Res. IR Spectroscopy in Solid pH_2

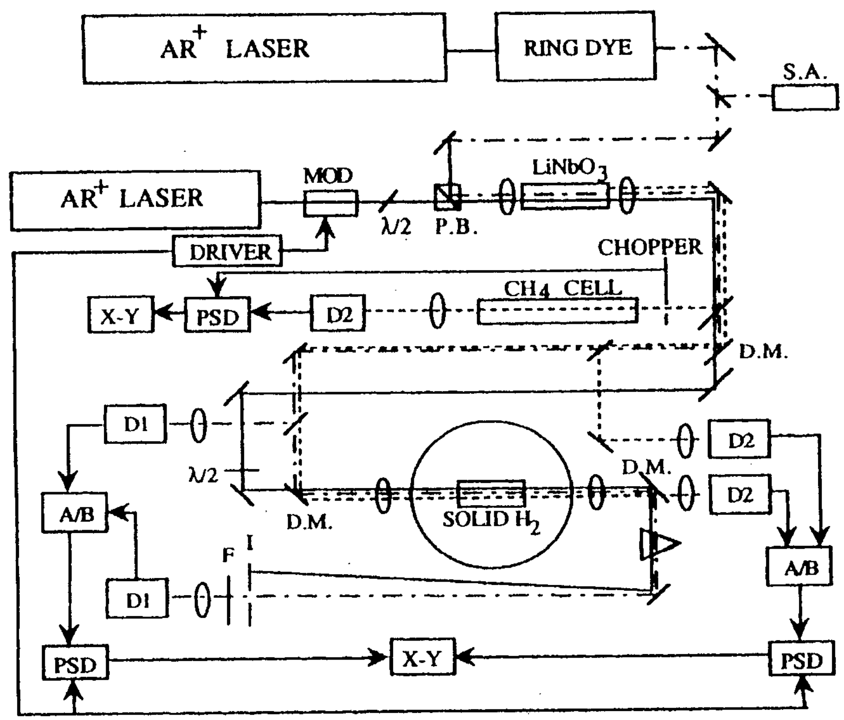
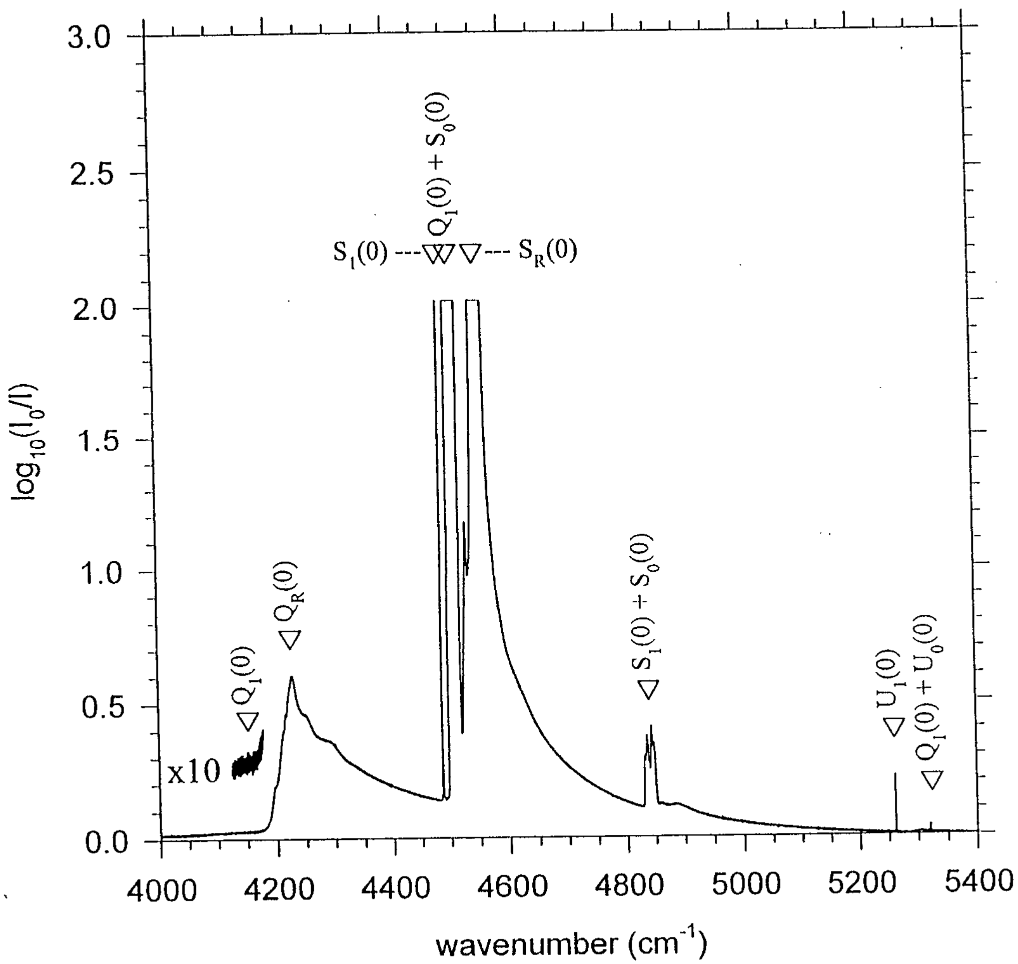


FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of $LiNbO_3$ is used for the former and that of solid H_2 is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.

[T. Momose, K.E. Kerr, D.P. Weliky, C.M. Gabrys, R.M. Dickson and T. Oka, J. Chem. Phys. **100**, 7840 (1994)]

IR Absorption of 6 mm Thick pH_2 Solid



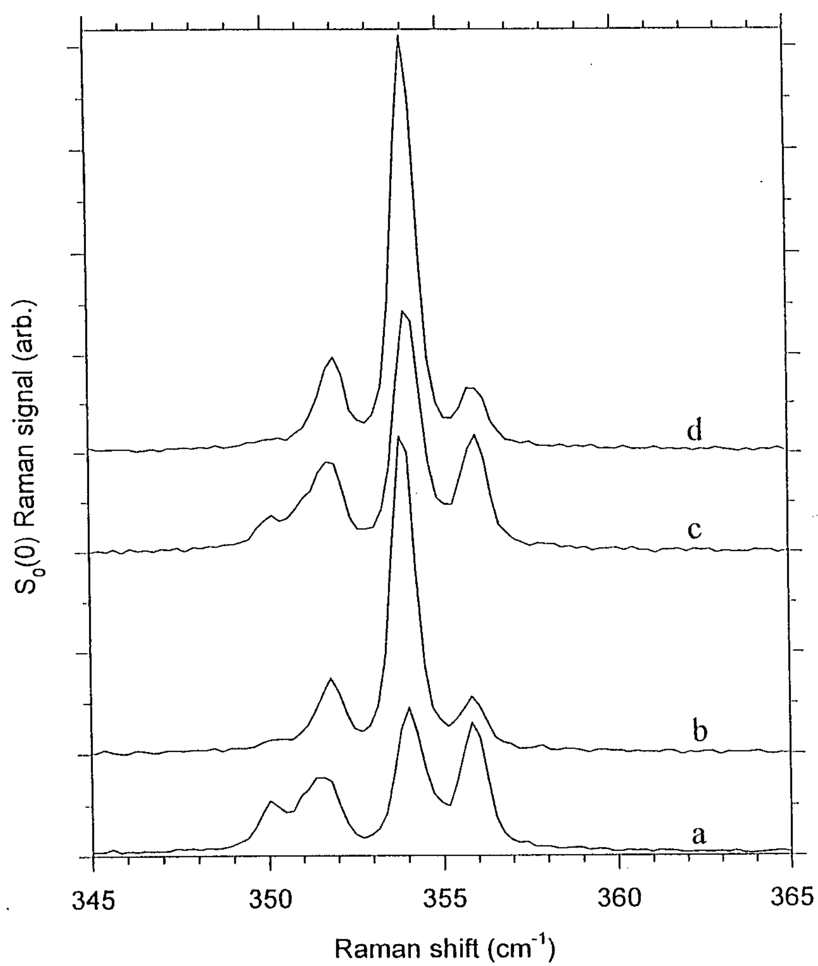
M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).

Non-observation of the $Q_1(0)$ transition demonstrates the absence of oH_2 impurities, and that the microscopic structure is not amorphous or porous.

Observation of $S_1(0)$ transition demonstrates the absence of inversion symmetry for <u>some</u> H_2 molecular environments.

[van Kranendonk and Gush, Phys. Lett. **1**, 22 (1962)]

Raman Spectra of pH_2 Solids



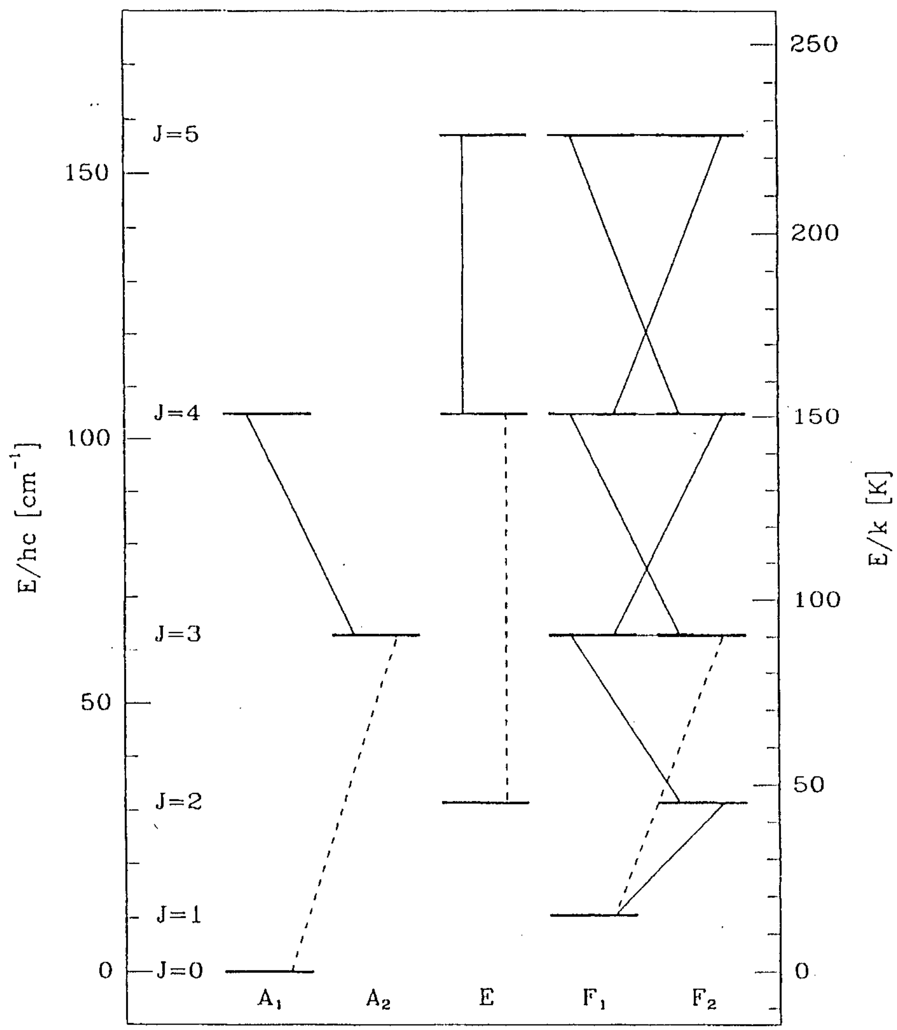
M.E. Fajardo and S. Tam,
J. Chem. Phys. **108**, 4237 (1998).

Mixed hcp/fcc as-deposited structure, anneals to hcp; compare with: [G.W. Collins, et al., Phys. Rev. B **53**, 102 (1996)].

(d) sample in (c) warmed to 4.5 K.
(c) 4.5 mm sample as deposited at 3.3 K ($\Phi = 290$ mmol/hr).

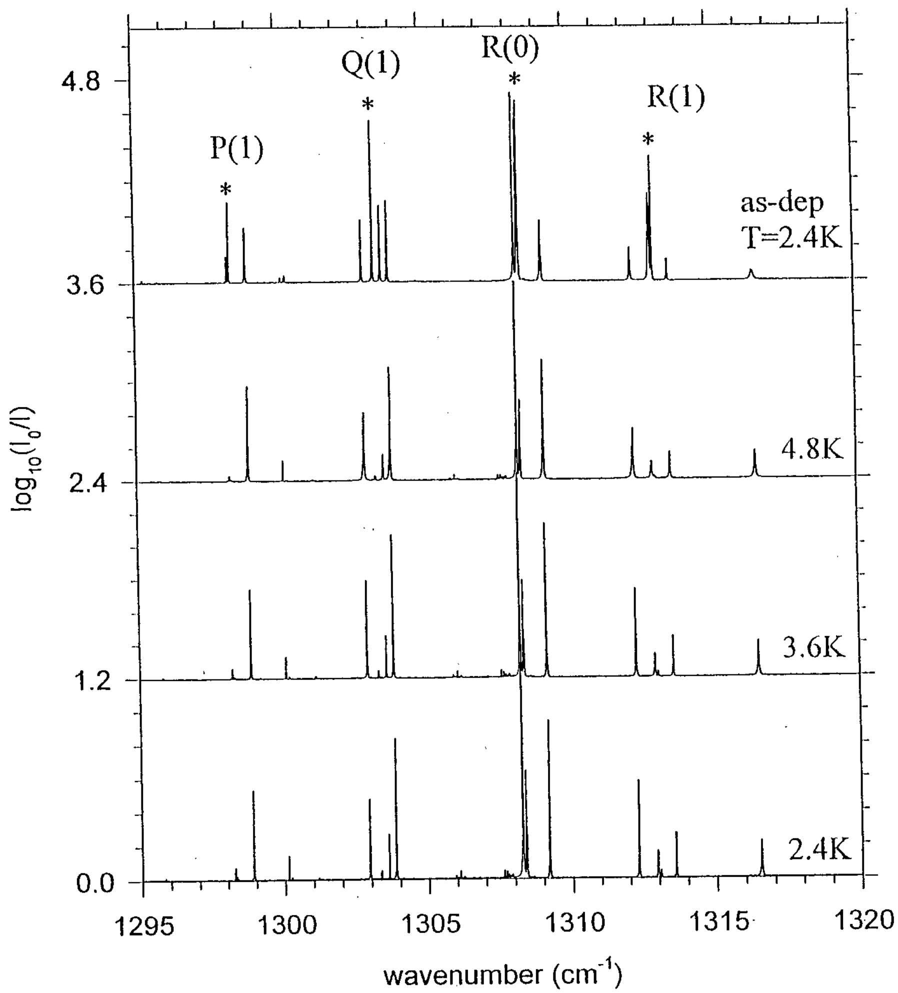
(b) sample in (a) warmed to 4.5 K.
(a) 6 mm sample as deposited at 3.1 K ($\Phi = 200$ mmol/hr).

CH_4 Nuclear Spin Modifications



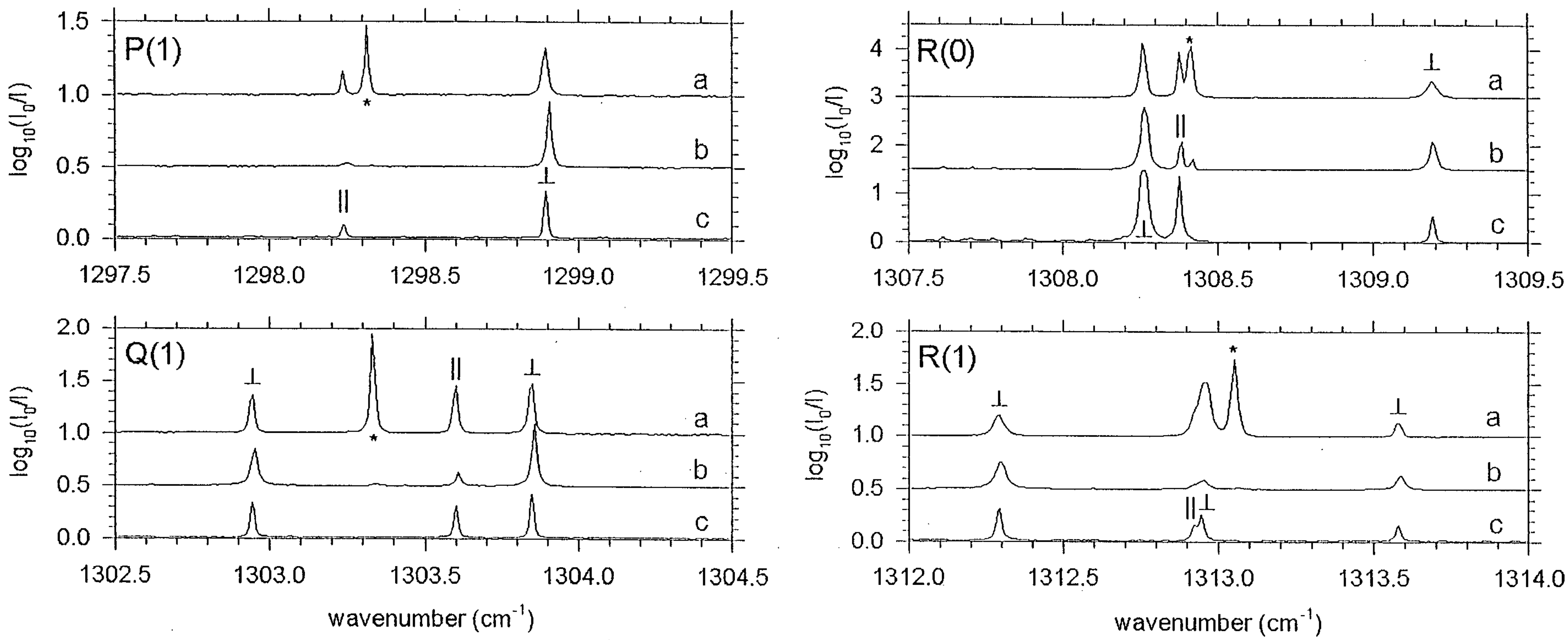
[M. Hepp, G. Winnewisser, and K.M.T. Yamada, J. Mol. Spectr. **164**, 311 (1994)]

ν_4 CH_4/pH_2 IR Absorptions (res = 0.01 cm^{-1})



S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabayashi, and T. Momose, J. Chem. Phys. **111**, 4191 (1999).

ν_4 CH_4/pH_2 IR Absorptions



(a) Rapid Vapor Deposited sample: as-deposited at 2.4 K

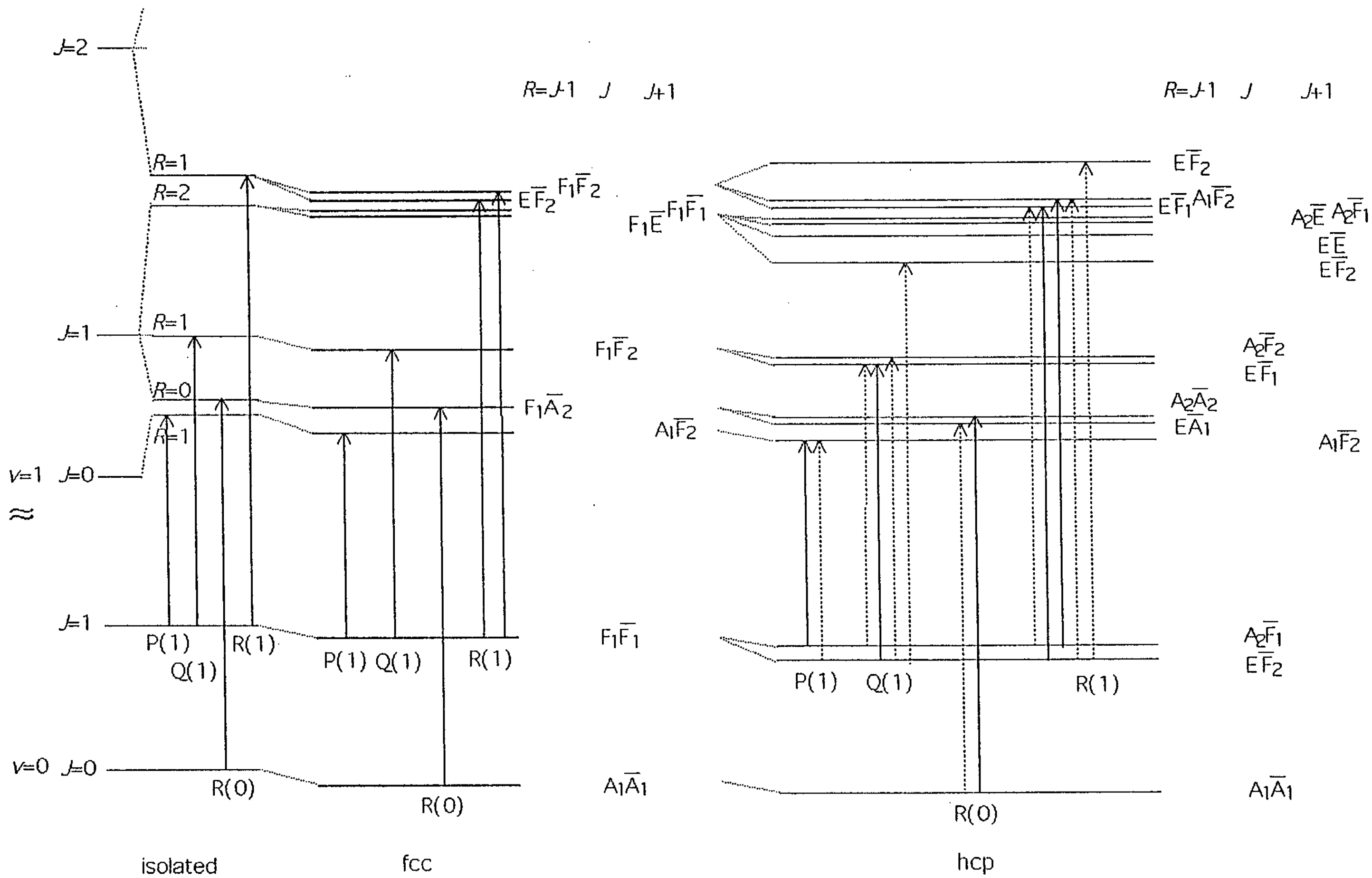
(b) Rapid Vapor Deposited sample: annealed to 4.8 K

(c) Enclosed Cell Condensed sample: cooled to 4.8 K

S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabayashi, and T. Momose, J. Chem. Phys. **111**, 4191 (1999).

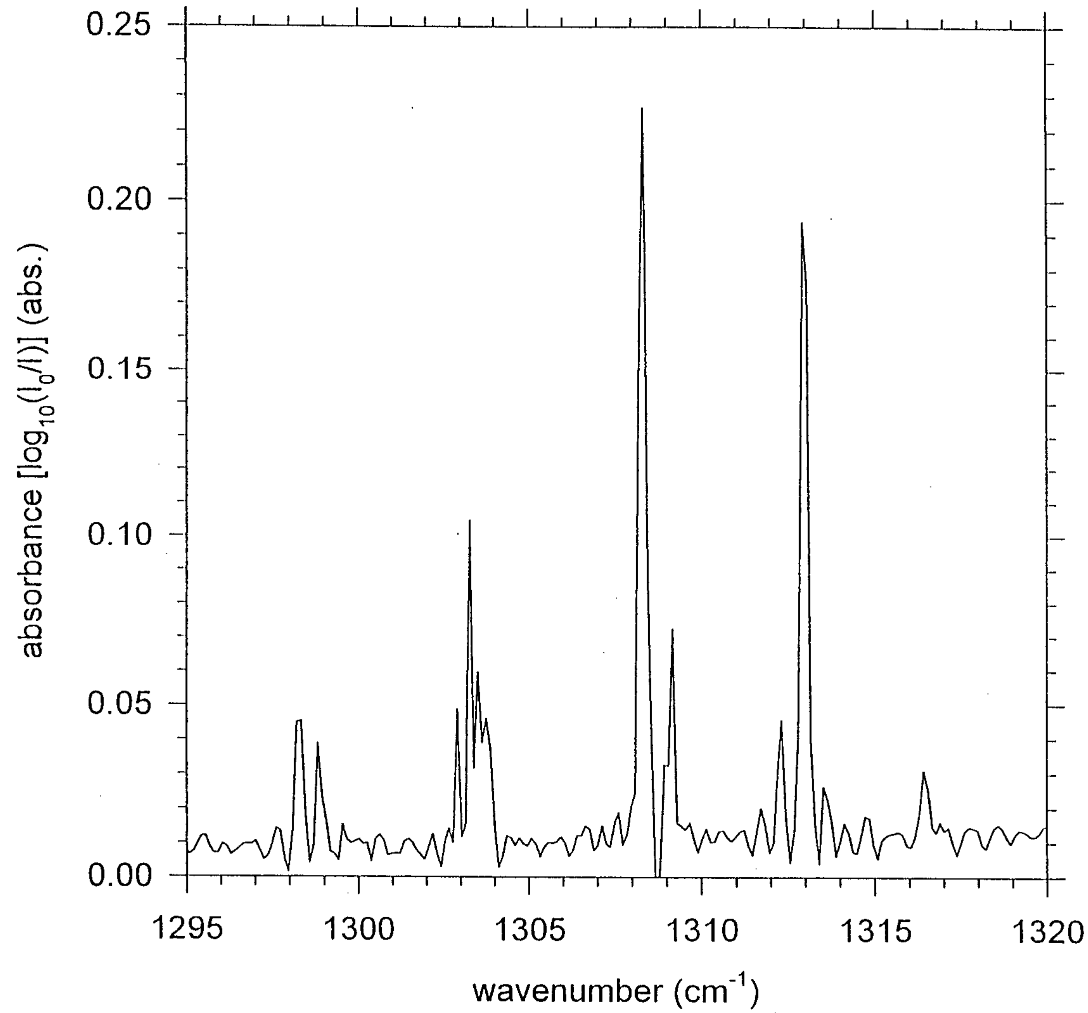
Department of Chemistry, University of Wyoming, Laramie, WY, 20 April 2001

ν_4 CH_4/pH_2 Energy Levels

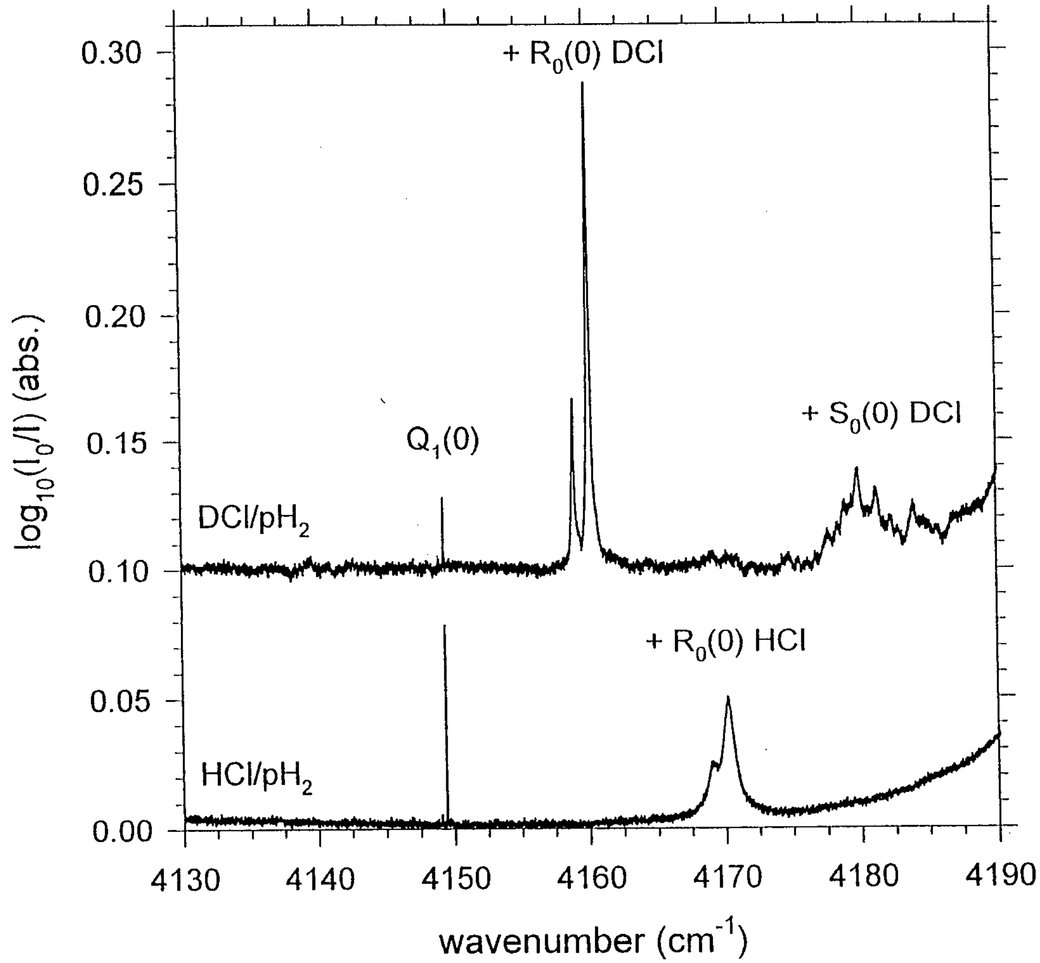


S. Tam, M.E. Fajardo, H. Katsuki, H. Hoshina, T. Wakabayashi, and T. Momose, J. Chem. Phys. **111**, 4191 (1999).

CH_4/pH_2 from Laser Ablation of Graphite

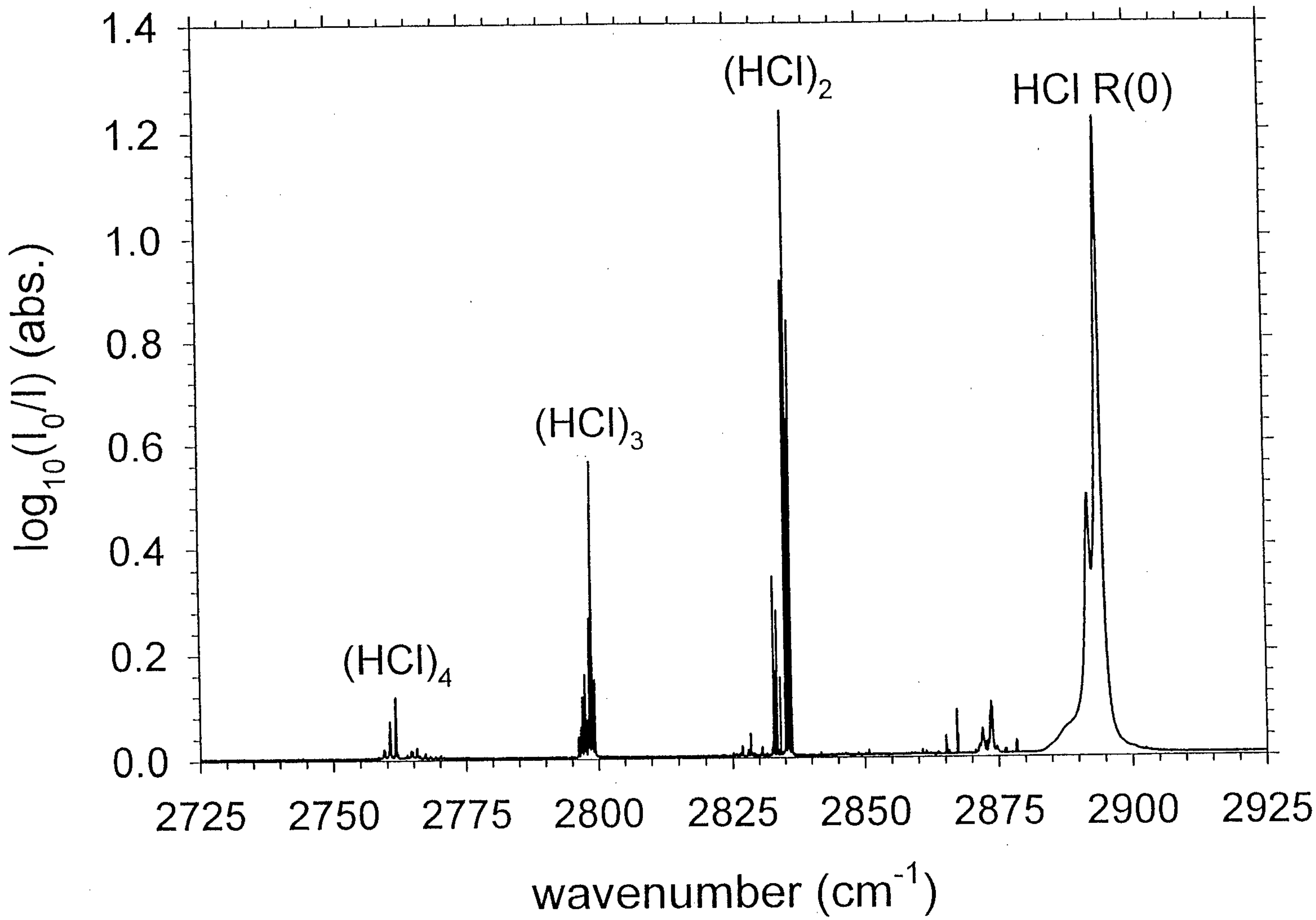


Co-operative IR absorptions



analysis in collaboration with D.T. Anderson, U. Wyoming and R.J. Hinde, U. Tennessee, Knoxville.

88 PPM HCl/pH_2



Department of Chemistry, University of Wyoming, Laramie, WY, 20 April 2001

Gas Phase $(HCl)_2$

High resolution, jet-cooled infrared spectroscopy of $(HCl)_2$: Analysis of ν_1 and ν_2 HCl stretching fundamentals, interconversion tunneling, and mode-specific predissociation lifetimes

Michael D. Schuder,[a] Christopher M. Lovejoy,[b] Robert Lascola,[c] and David J. Nesbitt[d]
Joint Institute for Laboratory Astrophysics, National Institute of Standards and Technology and University of Colorado, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

(Received 5 April 1993; accepted 7 June 1993)

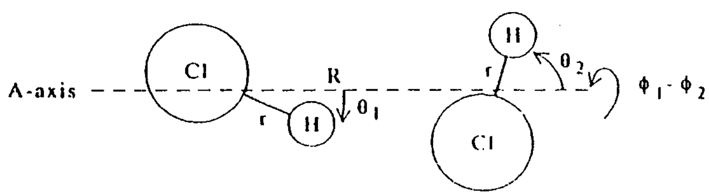
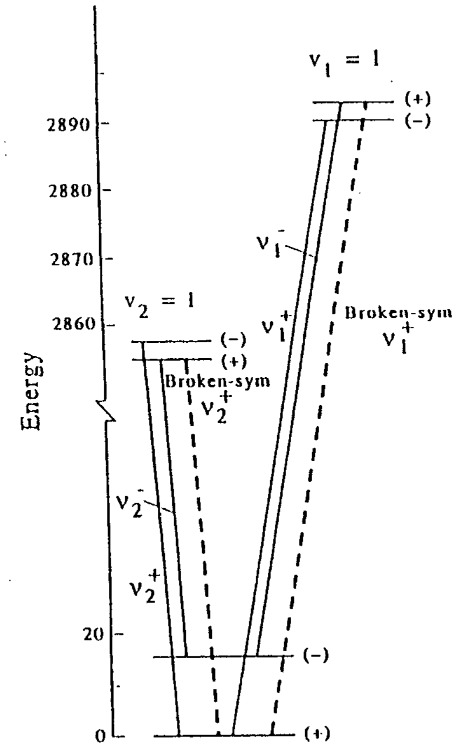
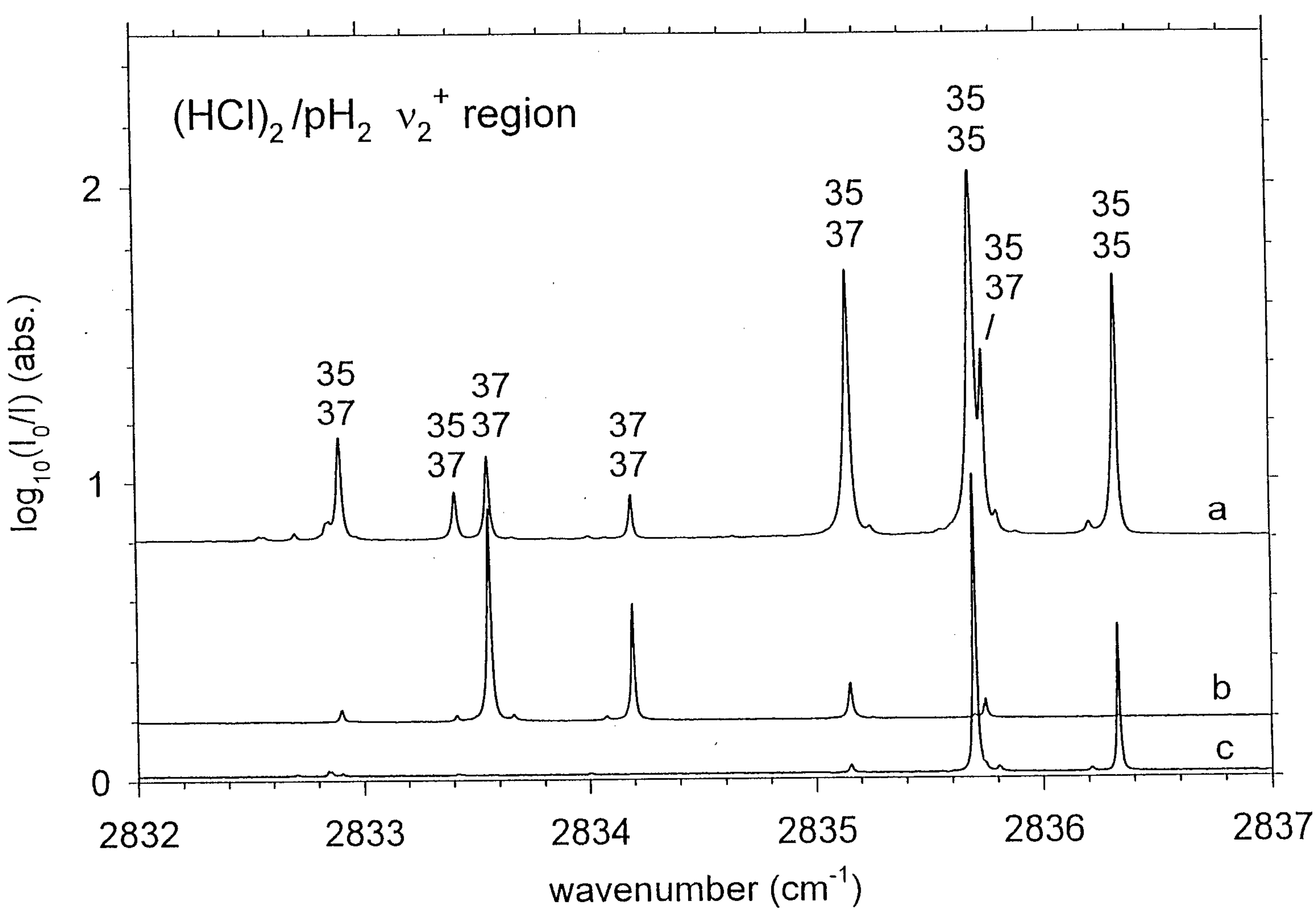


FIG. 1. Vibrationally averaged structure and internal coordinates for HCl dimer. The intermolecular axis R connects the HCl centers of mass. The internal angles, θ_1 and θ_2, are measured from the intermolecular axis to the HCl bonds r. The torsion angle, $\phi = \phi_1 - \phi_2$, is shown at 180° (planar). The minimum energy configuration shown is for $\theta_1 = 16°$, $\theta_2 = 87°$ with $\phi_1 - \phi_2 = 180°$. The HCl subunit on the left is referred to as the bonded HCl with an associated vibration labeled ν_2. The proton on the other HCl is not involved with the hydrogen bond, and this subunit is referred to as the free HCl, with a vibration labeled ν_1.



J. Chem. Phys. v99, p4346 (1993).

$(HCl)_2/pH_2$ isotopomers



analysis in collaboration with D.T. Anderson, U. Wyoming.

HEDM Cryosolids Accomplishments

(a list of "things that'll never work.")

* Trapped Li, B, Na, Mg, Al atoms in solid hydrogen at $T \approx 2$ K; attempts to demonstrate useful chemical energy storage still in progress
* Demonstrated production of gram-scale optically <u>transparent</u> pH_2 solids by rapid vapor deposition.
* Demonstrated that vapor deposited pH_2 solids are densest close-packed solids, NOT amorphous.
* Demonstrated suitability of vapor deposited pH_2 solids as hosts for high resolution IR absorption spectroscopy of chemically interesting dopants; spectral assignments ongoing.
* Generalized phenomena of dopant-induced and co-operative IR absorptions to chemically interesting dopants.